PHYSICAL REVIEW B VOLUME 32, NUMBER 2 15 JULY 1985

Raman scattering by intervalley carrier-density fluctuations in *n*-type Ge: Uniaxial stress and resonance effects

G. Contreras,[*] A. K. Sood,[†] and M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 22 February 1985)

We report the observation of light scattering by intervalley density fluctuations in *n*-type germanium. This scattering appears as a Lorentzian tail near the exciting laser frequency extending up to $\sim 500\ \mathrm{cm}^{-1}$. Application of a uniaxial stress of 15 kbar along [111] results in the disappearance of this scattering, thus confirming the assignment to intervalley fluctuations. The effect has been shown to resonate near the E_1 interband gap of Ge (~ 2.1 eV). An analysis of the dependence of the scattering on photon wavelength suggests that the effect is due mainly to intravalley diffusion and not to intervalley scattering.

I. INTRODUCTION

Light scattering by intervalley carrier-density fluctuations has been studied in detail in *n*- and *p*-type Si (Refs. 1–4) and is theoretically related to intervalley scattering[5] and intravalley diffusion[6] of the free carriers (see our preceding paper, Ref. 2, hereafter referred to as paper I). Attempts to observe this effect in *n*-type Ge have thus far failed, although the somewhat related phenomenon of scattering between valley-orbit-split impurity levels in the nondegenerate regime has been seen by Doehler *et al.*[7]

We report here the observation of a low-frequency Lorentzian scattering tail in heavily doped *n*-type Ge ($N_e \approx 1.6\times 10^{19}\ \mathrm{cm}^{-3}$). The effect is only significant for laser frequencies in the neighborhood of the E_1 gap of Ge [2.1 eV at 300 K and 2.2 eV at 100 K (Ref. 8)] and resonates strongly at E_1. Application of a compressive uniaxial stress along [111] should remove the valley degeneracy and bring all the carriers into the singlet [111] valley along the direction of the stress. Scattering by intervalley density fluctuations should then disappear. We have performed such experiments and shown that the low-frequency scattering indeed nearly disappears for an applied stress of 15 kbar. This confirms the assignment of the low-frequency tail observed in *n*-type Ge to scattering by intervalley density fluctuations. Similar experiments with a [100] stress have yielded analogous results for *n*-type Si, where the electron valleys are along [100] (Ref. 1).

The density-fluctuation mechanism for the scattering observed in *n*-type Si was shown in Paper I to be due, in part, to intervalley scattering[5] and, in part, to intravalley diffusion between neighboring points in space.[6] The latter is a nonlocal effect proportional to the square of the scattering vector **q**.[6] We have studied the dependence on **q** of the phenomenon reported here for *n*-type Ge and shown that the width of the scattering band varies like q^2. Hence, in this case nonlocal intravalley diffusion seems to be the dominant mechanism responsible for the intervalley fluctuations observed in the Raman spectra.

II. THEORY

The expressions for the light scattering efficiency[5,6,9] by carrier-density fluctuations in *n*-type Ge is similar to that of *n*-type Si with the difference that the summation in Eq. (2) (Paper I) runs from 1 to 4 and $A_0 = 4\tau_{\mathrm{inter}}^{-1}$. These changes reflect the fact that Ge has four equivalent valleys rather than six (three pairs) for Si.

Upon application of a uniaxial stress along the [111] direction the electron valleys of *n*-type Ge split into a singlet along the [111] direction of **k** space (lower in energy) and the $[\bar{1}\,\bar{1}\,1]$, $[\bar{1}1\bar{1}]$, $[1\,\bar{1}\,\bar{1}]$ triplet (higher in energy). The energy splitting between singlet and triplet can be written as[10]

$$\Delta = E_S - E_T = \tfrac{4}{9} S_{44} \Xi_u X \ , \tag{1}$$

where S_{44} is the elastic compliance constant, $\Xi_u = 15.9$ eV (Ref. 10) a deformation potential, and X the magnitude of the applied stress. The split valleys repopulate themselves so as to equalize the Fermi energies. The populations of the singlet and triplet valleys, N_S and N_T, and the new Fermi energy are found by solving the set of equations

$$\begin{aligned} &N_e = N_S + 3N_T \ , \\ &N_S = \int_0^\infty N_d(E) f(E-\eta)\,dE \ , \\ &N_T = \int_0^\infty N_d(E) f(E-\eta-\Delta)\,dE \ , \end{aligned} \tag{2}$$

where f is the Fermi function, η the Fermi energy measured from the bottom of the singlet valley, and $N_d(E)$ is the density of states of one valley, with the energy measured from the bottom of the valley,

$$N_d(E) = \frac{2^{1/2}(m_{\parallel} m_{\perp}^2)^{1/2}}{\pi^2 \hbar^3} E^{1/2} \ . \tag{3}$$

Equation (2) can be solved for η and thus for N_S and N_T versus X by using the tabulated values of the Fermi integrals.[11]

For the case of valleys with different carrier concentrations N_α, such as that of *n*-type Ge under stress, Eq. (2) of Paper I must be replaced by[5]

$$B(X)=\frac{\hbar e^4}{\pi c^4}\sum_{\alpha=1}^{4}\frac{dN_\alpha}{d\eta}\left|\hat{\mathbf{e}}_L\cdot\left[\frac{1}{\underset{\sim}{m}_\alpha}-\left[\frac{dN_e}{d\eta}\right]^{-1}\sum_{\alpha'=1}^{4}\frac{1}{\underset{\sim}{m}_{\alpha'}}\frac{dN_{\alpha'}}{d\eta}\right]\cdot\hat{\mathbf{e}}_S\right|^2 , \tag{4}$$

where we implicitly assume for simplicity that A, i.e., the intervalley scattering plus the intravalley diffusion mechanisms, does not vary with stress (the quality of our present data at high stresses is not sufficient to detect the corresponding variation). It is easy to see in Eq. (4) that $B(X)\rightarrow 0$ for large X (i.e., for X such that $\Delta \gg \eta$), as expected.

Implicit in the discussion above is the assumption that the laser and scattered frequencies ω_L and ω_S are much smaller than those of the direct gaps at the point of **k** space where the electrons are placed (L point for n-type Ge). In this case, the energy denominator of interband transitions responsible for the scattering can be transformed into the effective masses of Eq. (4).[12] In our experiments for n-type Ge we have been able to observe electronic scattering only near resonance, i.e., only when the laser frequency lies near the spin-orbit-split E_1 ($\sim$2.1 eV at 300 K) and $E_1+\Delta_1$ ($\sim$2.3 eV at 300 K) critical points. In this case the mass $m_\perp$ in units of m_e must be replaced in Eq. (4) by

$$\left[\frac{1}{m_\perp}\right]_{\text{eff}}\simeq 1+\frac{\hbar^2P^2}{m_e}\left|\frac{\omega_1}{\omega_1^2-\omega_L^2+2i\Gamma\omega_1}+\frac{\omega_1+\Delta_1}{(\omega_1+\Delta_1)^2-\omega_L^2+2i\Gamma'(\omega_1+\Delta_1)}\right| , \tag{5}$$

where P is the matrix element of the momentum operator between the top valence band (L_3) and the bottom of the conduction band (L_1) at L. $\Gamma(\Gamma')$ represents the Lorentzian broadening of the gap $E_1(E_1+\Delta_1)$. From $m_\perp=0.08m_e$ one finds $\hbar^2P^2/m_e\simeq 13$ eV. At room temperature $\omega_1=2.1$ eV, $\Delta_1=0.19$ eV, $\Gamma=0.06$ eV, and $\Gamma'=0.08$ eV. At 80 K $\omega_1=2.2$ eV, $\Delta_1=0.19$ eV, $\Gamma\simeq 0.04$ eV, and $\Gamma'=0.05$ eV.[8]

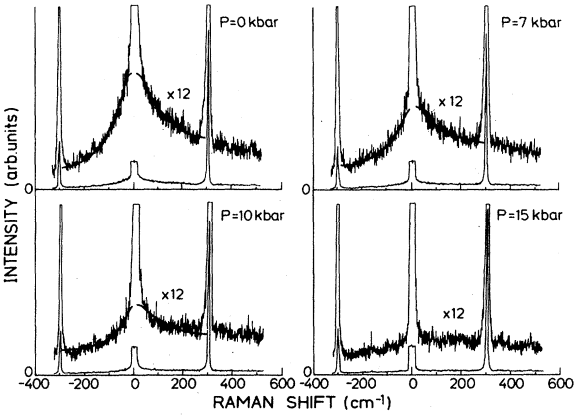

FIG. 1. Pressure dependence of the electronic light scattering tail of n-type Ge with $N_e=1.6\times10^{19}$ cm^{-3}. The solid lines in each spectrum are fits to the anti-Stokes and Stokes sides with Eq. (1) of Paper I. All the spectra shown were measured at $T=300$ K, using the 6471-Å line of the Kr$^+$ laser, with the scattering configuration of $\hat{\mathbf{e}}_L\|[111]$, $\hat{\mathbf{e}}_S\|[11\bar{2}]$, and with the $[1\bar{1}0]$ direction as the scattered face. The pressure was applied uniaxially along [111]. The sample was in vacuum ($\sim10^{-2}$ Torr) to avoid rotational Raman lines of nitrogen.

An evaluation of Eq. (5) for the parameters given above yields $(1/m_\perp)_{\text{eff}}=52$ at $T=300$ K for $\omega_L=1.92$ eV (6471 Å). Using the critical-point parameters found at 80 K (Ref. 8) we obtain $(1/m_\perp)_{\text{eff}}=39$ at the same frequency. These numbers correspond to a resonance enhancement of the effective masses by 4.2 and 3.1 at 300 and 80 K, respectively, with respect to the off-resonance value $(1/m_\perp)=12.5$. The corresponding resonance enhancement of the electronic *scattering efficiencies* is the square of the enhancement given above.

III. EXPERIMENT

The Raman spectra reported here were measured in the backscattering geometry using a 1-m SPEX double monochromator equipped with a photon-counting photomultiplier detector system. We used the 6764-, 6471-, and 5682-Å exciting lines of a Kr$^+$ laser. For the uniaxial pressure experiments at room temperature (and under vacuum $\sim10^{-2}$ Torr) we used a stress apparatus described elsewhere,[13] which allowed the application of up to $\sim$20-kbar compressional stresses. The samples used for the pressure experiments were cut from single crystals of n-type Ge with typical dimensions $15\times1.2\times1.2$ mm^3. The stress was applied along the [111] axis which was parallel to the long dimension of the sample. The scattering measurements were performed on $(1\bar{1}0)$ faces which had been mechanically polished to optical flatness with 0.3 alumina, followed by polishing with Syton (Monsanto Chemical Company) and a final treatment with HF. The carrier concentration was determined from the minimum in the ir reflectivity spectra ($N_e=1.6\times10^{19}$ cm^{-3}).[14]

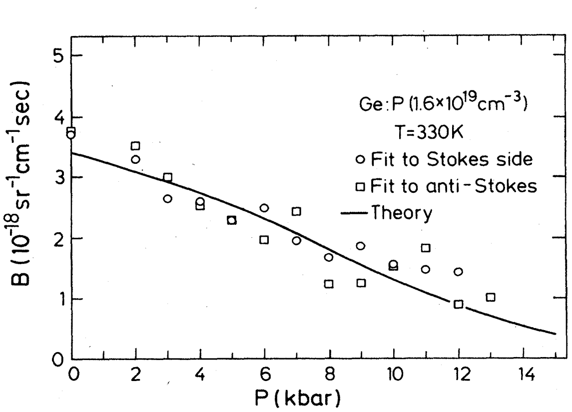

FIG. 2. Pressure dependence of the intensity factor B found experimentally for the sample of Fig. 1. The solid line represents the fit with Eq. (6) to the experimental points using a scaling factor as an adjustable parameter.

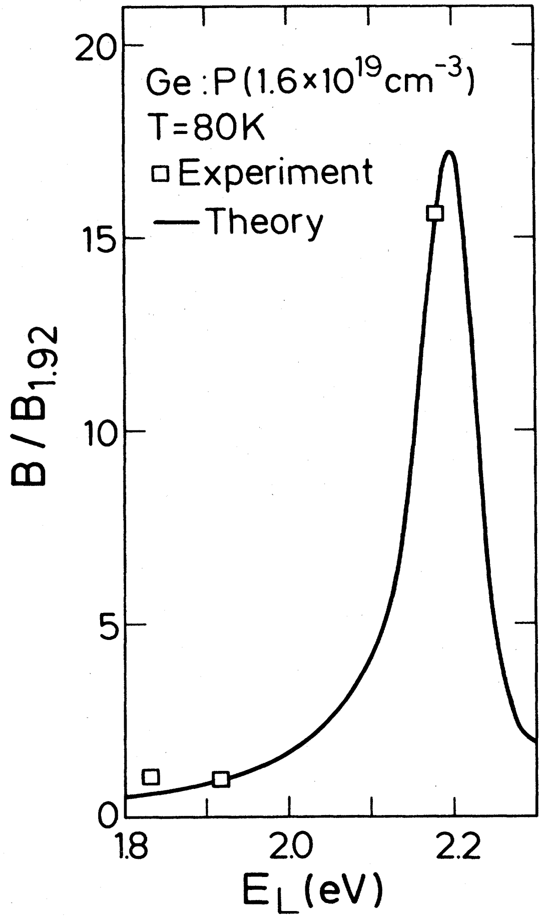

FIG. 3. Resonance behavior of the intensity factor B, relative to that at 6471 Å (1.92 eV). The solid line represents the theoretical resonance predicted with Eq. (5). The scattering configuration used is $\hat{e}_L \| [001]$, $\hat{e}_S \| [010]$, with [100] direction normal to the scattering face. In this configuration there may be a small contribution of spin-flip scattering (Γ_{15} symmetry, Refs. 9 and 12) to the light scattering mechanisms which will be discussed in a forthcoming publication.

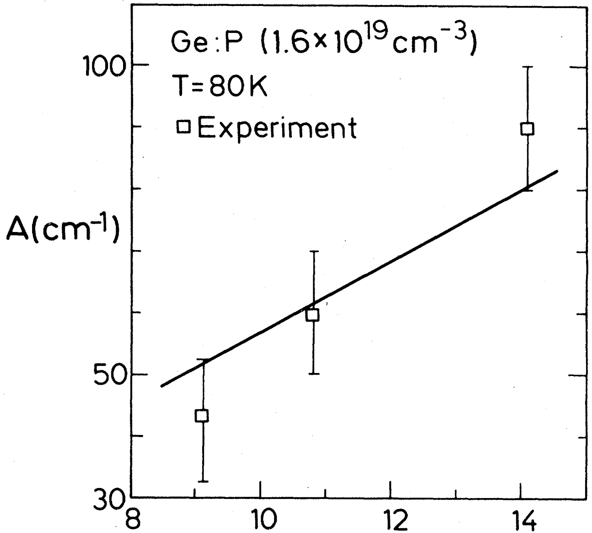

FIG. 4. Dependence of the Lorentzian parameters A on the square of the scattering vector $\mathbf{q}$ obtained for the sample of Fig. 3. The solid line is a fit with a straight line passing through the origin.

IV. RESULTS AND DISCUSSION

Typical spectra for scattering by charge-density fluctuations are shown in Fig. 1. These spectra are characterized by a low-frequency tail having a Lorentzian shape as described by Eq. (1) of Paper I. The solid lines in Fig. 1 represent a fit with this equation using A and B as adjustable parameters. All these spectra were taken at 300 K with the 6741-Å line of the Kr$^+$ laser in a $\Gamma_{25'}$ configuration, i.e., $\hat{e}_L$, $\hat{e}_S$ parallel to the [111] and [11$\bar{2}$] axes, respectively, for a [1$\bar{1}$0] scattering face. In the spectra taken with the sample under pressure, we note a decrease and, at the highest pressure, a total disappearance of the tail which corresponds to the predictions of Eq. (4). In fact, according to Eq. (4) the value of B for the scattering configuration we used is

$$B = \frac{\hbar e^4}{\pi c^4} \frac{4}{3} \left[\frac{1}{3m_\perp} \right]^2_{\text{eff}} \frac{dN_{\alpha T}}{d\eta} , \qquad (6)$$

where $N_{\alpha T}$ is the electron concentration in one of the triplet valleys (note that the singlet does not contribute to B for this configuration). For large values of X (~ 15 kbar) these triplet valleys become completely depopulated and the tail should disappear in accordance with Fig. 1. The absolute values of B were obtained experimentally by comparison with the $\Gamma_{25'}$-Raman phonon of Ge, whose absolute scattering efficiency was known.[15] Figure 2 shows the dependence of B on pressure. The solid line represents the best fit of the calculated values [using Eq. (6)] and taking into account the resonance enhancement of $(m_\perp)^{-1}_{\text{eff}}$ to the experiment with an adjustable multiplicative factor. The multiplicative factor was found to be 6: the theoretical values are lower than the experimental ones. Despite the discrepancy in the absolute values of theory and experiment (a factor of 6), the shape of the experimental dependence on pressure is reproduced well by the theory.

In order to confirm the resonance behavior of the inverse of the transverse mass discussed above [Eq. (5)], we perform measurements with the 6764-, 6471-, and 5682-Å lines of the Kr$^+$ laser. The corresponding photon energies are below E_1 and $E_1+\Delta_1$ at liquid-nitrogen temperature. In this manner we avoid spurious contributions to the electronic scattering tail from the $E_1-E_1+\Delta_1$ luminescence of n-type Ge.[16] Figure 3 displays the resonance behavior measured for B, relative to the 6471-Å (1.92-eV) line of the Kr$^+$ laser. The solid line was calculated with Eq. (5). Good agreement between the theoretical prediction and the experimental resonance enhancement of B was found.

The dependence of the Lorentzian width parameter A on the square of the scattering wave vector q is presented in Fig. 4. The solid line in this plot represents a fit with a straight line intercepting the origin. In fact, this line should go through the origin if no local intervalley scattering is present (see Paper I). A fit to the experimental points without this constraint yields a negative intercept with the y axis, which is physically impossible since the intercept A_0 represents the (*positive*) intervalley scattering frequency. The best fit with a non-negative intercept is that which goes through the origin and thus corresponds to zero local intervalley scattering. The intervalley scattering frequency A_0 can, in principle, be calculated with Eqs. (4), (6), and (11) of Paper I and the fact that $A_0=4\tau_{\text{inter}}^{-1}$. An evaluation of A_{02} [Eq. (4) of Paper I] yields the values 0.14 and 0.84 cm^{-1}, respectively, for phonons of $\omega_i=83$ and 222 cm^{-1} using the corresponding values of the electron-phonon coupling constants 2×10^7 eV/cm and 3×10^8 eV/cm, given in Ref. 17 for Ge. The calculation of A_{01}, with Eq. (6) of Paper I, yields the value $A_{01}=1.1$ cm^{-1}. Thus, we find total values of A_0 around 2 cm^{-1}, which are negligible in comparison with the total A's observed experimentally ($A>40$ cm^{-1}), in agreement with the conclusions reached above.

V. CONCLUSIONS

We have observed a tail in the low-frequency scattering spectrum of heavily doped n-type Ge which, in view of its behavior upon application of a uniaxial stress along [111], can be attributed to scattering by electronic intervalley density fluctuations. This scattering has been observed to resonate at the E_1 gap of Ge. The Lorentzian width of the scattering tail has been shown to be mainly due to nonlocal scattering by intravalley diffusion.

Note added in proof. Recently we have observed in n-type Ge scattering by spin-density fluctuations. The selection rules are given by $|\hat{e}_L\times\hat{e}_S|^2$. The scattering thus appears for crossed incident and scattered polarizations. It resonates near E_1 and its strength is about one-third of the one reported here [N. Mestres and M. Cardona (unpublished)].

ACKNOWLEDGMENTS

Thanks are due to I. P. Ipatova and her Leningrad coworkers for illuminating discussions and their interest in this work. The expert technical help of H. Hirt, M. Siemers, and P. Wurster is also gratefully acknowledged. G.C. acknowledges financial support from the Deutscher Akademischer Austauschdient.

---

[*] Permanent address: Escuela Superior de Física y Matemáticas—Instituto Politécnico Nacional, Edificio 6, Unidad Profesional Adolfo López Mateos, Delegacion G.A. Madero, 07300 México, Distrito Federal, México.

[†] Permanent address: Materials Science Laboratory, Reactor Research Centre, Kalpakkam—603102, India.

[1] M. Chandrasekhar, M. Cardona, and E. O. Kane, Phys. Rev. B **16**, 3579 (1977).

[2] G. Contreras, A. K. Sood, and M. Cardona, preceding paper, Phys. Rev. B **32**, 924 (1985).

[3] G. Contreras, A. K. Sood, and M. Cardona, in *Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by J. Chadi and W. A. Harrison (Springer, New York, in press).

[4] M. Chandrasekhar, U. Rössler, and M. Cardona, Phys. Rev. B **17**, 1623 (1978).

[5] I. P. Ipatova, A. V. Subashiev, and V. A. Voitenko, Solid State Commun. **37**, 893 (1981).

[6] I. P. Ipatova, A. V. Subashiev, and V. A. Voitenko, J. Raman Spectros. **10**, 221 (1981).

[7] J. Doehler, P. J. Colwell, and S. A. Solin, Phys. Rev. Lett. **34**, 584 (1975); J. Doehler, Phys. Rev. B **12**, 2917 (1975).

[8] L. Viña, S. Logothetidis, and M. Cardona, Phys. Rev. B **30**, 1979 (1984).

[9] M. Cardona, in *Light Scattering in Solids IV,* Vol. 54 of *Topics in Applied Physics,* edited by M. Cardona and G. Güntherodt (Springer, Heidelberg, 1984), p. 121.

[10] I. Balslev, Phys. Rev. **143**, 636 (1966); Phys. Lett. **24A**, 113 (1967).

[11] V. I. Fistul, *Heavily Doped Semiconductors* (Plenum, New York, 1969).

[12] M. Cardona, in *Light Scattering in Solids II,* Vol. 50 of *Topics in Applied Physics,* edited by M. Cardona and G. Güntherodt (Springer, Heidelberg, 1984), p. 103.

[13] H. Vogelmann and T. A. Fjeldly, Rev. Sci. Instrum. **45**, 309 (1974).

[14] P. A. Schumann, Jr., Solid State Technol. **13**, 50 (1970).

[15] A. K. Sood, G. Contreras, and M. Cardona, Phys. Rev. B **31**, 3760 (1985).

[16] G. Contreras, A. Compaan, J. Wagner, M. Cardona, and A. Axmann, J. Phys. (Paris) Colloq. **44**, C5-55 (1983).

[17] L. Reggiani, J. Phys. Soc. Jpn. Suppl. A **49**, 317 (1980).